

PATENT SPECIFICATION

DRAWINGS ATTACHED

Inventor: FRANCIS JOHN LONG

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International Classification:—B01j. C08f.

COMPLETE SPECIFICATION

Emulsion Polymerisation Apparatus

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides an apparatus in which continuous emulsion polymerisation may be carried out.

Our invention provides a continuous emulsion polymerisation apparatus which comprises a reaction vessel fitted with a stirrer of the type hereinafter described, which vessel is equipped, adjacent to the stirrer, with inlets for fine streams of fluid and with an outlet.

The stirrer for use in this invention is designed to produce mainly rotational movement of the liquid in the reaction vessel, the geometry of the stirrer and vessel being such that a pattern of Taylor rings is produced in a liquid in the vessel when the stirrer is in use. The term "Taylor rings" is used to denote a particular flow pattern, such a flow pattern being one in which the stirred liquid under consideration is segmented in planes perpendicular to the principal axes of the vessel, and of rotation of the stirrer, with much higher rates of mass transfer within than between such segments and well defined boundaries separating the segments. Suitable forms of stirrer which provide these conditions include, for example, cylindrical or cone shaped stirrers, and stirrers made from discs, segmented discs, annular rings and the like, spaced regularly or irregularly on a shaft. Conveniently the inlets may be adja-

cent to opposite ends of the stirrer and they may in fact be ports in a hollow stirrer which itself acts as a conduit for the fluids to be added to the reaction vessel. These arrangements enable fluids entering the vessel to be dispersed rapidly in the Taylor rings.

In a preferred form of our apparatus the reaction vessel is a vertical cylinder and the outlet is at the bottom of the cylinder.

In one form of our invention the upper end of the reaction vessel is also equipped with a reflux condenser. In addition, or alternatively, the vessel may be fitted with a jacket through which heating or cooling fluid may be passed or with internal heating or cooling tubes. Cooling or heating may also be carried out by passing an appropriate fluid through a hollow stirrer. By fitting appropriate pressure-tight bearings and joints our apparatus may be modified for use for the polymerisation of monomers at super- or sub-atmospheric pressures.

In a further preferred form of our invention the stirrer consists of a plurality of discs or annular rings on a shaft, the design and peripheral speed of the stirrer being such that a number of Taylor rings is formed.

A preferred form of our apparatus is shown in the diagram accompanying the complete specification.

A cylindrical reaction vessel 1 is fitted with a rotating disc stirrer 2, supported on bearings 3 and 4. The stirrer 2 can be rotated by turning a shaft 5. The vessel 1 is equipped with upper and lower jets 7 and 6 respectively, an outlet 8 and a reflux condenser (not completely shown) 9. The vessel 1 is surrounded by a jacket 11 with entry and exit pipes 10 and 12. This jacket can be used

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to circulate fluid to supply or remove heat from the reaction vessel 1.

The dimensions of our apparatus are obviously dependent on the output of emulsion required and we have found that suitable stirring can be obtained when a cylinder stirrer of diameter 1.5 inches is rotated in a vessel of internal diameter 2.3 inches at between 500 and 1500 r.p.m. or a stirrer of 4 inches diameter in a vessel of 6 inches diameter at between 100 and 1000 r.p.m. The preferred speed for the larger stirrer is between 440 and 880 r.p.m.

The method of use of our apparatus can best be explained by actual examples of its use for the preparation of stable polymer emulsions. All parts are by weight in Examples I, II and III.

EXAMPLE I

With an apparatus substantially as shown in the diagram accompanying the provisional specification, an aqueous solution, containing 84 parts polyvinyl alcohol, 7.5 parts ammonium persulphate and 6 parts sodium carbonate in 1247 parts of water, was added to the vessel 1 through the jet 7. Vinyl acetate was added through the jet 6. By passing water

55	Solids - - - - -	42%
	Viscosity - - - - -	1.5—2 poise (Ultraviscoson)
	Particle size - - - - -	0.75—1.0 μ
	Average time of stay - - - - -	1 hr. 50 mins.

EXAMPLE III

The vessel was this time charged with 1 litre aqueous medium containing:—

(a) 242 parts of a 13% ammonium polymethacrylate solution in water.

25 parts Calsolene Oil (50% solution in water of sodium salt of sulphated methyl oleate).

and heated to 80° C. while the stirrer was rotated 600 r.p.m.

280 parts of an aqueous catalyst solution containing:—

(b) 25 parts Calsolene Oil.

5 parts 100 volume hydrogen peroxide solution.

250 parts water

were then added through jet 7 and pure methyl methacrylate monomer fed in at the lower jet 6 at 4.5 ml./min. After 1.5 hours further aqueous medium (a) to which had been added 20 ml. 100 volume hydrogen peroxide was fed at 3.75 ml./min. through jet 7.

After 3½ hours from catalyst solution addition, the creamy emulsion leaving the reactor contained 48.4% solids. The average particle size was about 0.75 μ and the viscosity 0.4 poise (Ultraviscoson).

EXAMPLE IV

A vessel similar to that shown in the diagram accompanying the complete speci-

through the jacket 11 the reactants were maintained at about 60° C.

The stirrer 2 was rotated at 600 r.p.m. and was breaking up the filamentary streams of reactants entering the vessel into fine particles. When the apparatus reached a steady state, i.e. material was flowing from the outlet 8 at the same rate as reactants were being added to the substantially full vessel, the constants of the emulsion emerging from the outlet 8 were determined. The rates of addition of monomer and solution at steady state were 3.6 and 3.75 parts/min respectively. The solids content of the polymer emulsion discharge from the outlet 8 was approximately 50% by weight, the monomer content 0.5% and the viscosity 2—3 poise (measured by an Ultraviscoson). The average particle size was 0.5 μ and the average time of stay was 2 hours 20 minutes.

EXAMPLE II

Example I was repeated this time with the speed of rotation of the stirrer increased to 1150 r.p.m. The flow rates into the vessel of monomer and solution were 3.7 parts and 6.2 parts/min. respectively. The constants of the product were:—

cation in which the vessel was 6 inches in diameter and equipped with a stirrer consisting of a vertical cylindrical shaft fitted with discs of 4 inches diameter mounted axially on the shaft and rotated at 660 r.p.m. was supplied with monomer and catalyst as described in Example III. The feed-rate of vinyl acetate monomer was 5.82 kg./hr. and of aqueous solution (containing polyvinyl alcohol 3.25% by weight, ammonium persulphate 0.5%, sodium carbonate 1.6%, water 94.65%) 4.35 kg./hr. On reaching the steady-state the product, with an average time of stay of 50 minutes, contained 55% by weight of solids, 2% of monomer. The average emulsion particle size was approximately 1.5 μ .

When a steady state has been reached in our preferred apparatus the mechanism of reaction is thought to be as follows. As stated earlier the streams from the jets are rapidly broken down to fine particles by the rotating stirrer. Now since the aqueous solution which enters via the upper jet is heavier than the monomer which enters through the lower jet countercurrent flow develops and polymerisation proceeds. This countercurrent movement of the reagents has the advantage that as the monomer is consumed by reaction during its movement up the vertical series of Taylor rings in the vessel it passes into regions of progressively higher catalyst con-

centration. Conditions of near uniformity of reaction rate thus obtain throughout the column which represent the most efficient use of the available reactor volume for reaction. Since the orifice of the jet 6 is substantially higher than the outlet 8, and conveniently is adjacent to the lowest Taylor ring, very little monomer is mixed with the product.

The polymer dispersion produced in our preferred apparatus on sinking past the orifice of the jet 6 is mixed with no further monomer and so any monomer mixed with it tends to polymerise or diffuse up the vessel before the dispersion passes through the outlet 8 at the bottom of the reaction vessel.

From the above it will be appreciated that many monomers can be polymerised in our apparatus provided suitable catalysts, flow rates, temperatures, pressures, and stirring speeds are chosen. Typical examples of these giving aqueous emulsions have been given in the examples. Others include such vinyl type monomers as styrene, vinyl toluene, vinyl and vinylidene chlorides and acrylonitrile, esters of acrylic and methacrylic acids such as methyl, ethyl, butyl methacrylate and ethyl acrylate, olefinic type monomers such as ethylene, propylene, butadiene and combinations of monomers to give copolymer emulsions such as styrene-butadiene and methyl methacrylate-butadiene. Alternatively, the apparatus may be used for emulsion polymerisation in non aqueous systems.

The design of suitable apparatus in which emulsion polymerisation may be carried out in accordance with our invention can be changed in various ways from that shown in the accompanying diagram. For example, it is possible to substitute for the fluid inlet jets shown sinter plates which produce fine streams of particles of fluid. The stirrer may be modified provided the stirring conditions detailed above still obtain, but the form detailed in Example IV where the particular design of stirrer concerned has the advantage of giving a greater volume available for reaction for given reactor dimensions and impresses upon the fluid a particularly desirable internal flow pattern, is preferred. By increasing the distance between the lower inlet and the outlet pipe, for example, by raising the lower jet relative to the stirrer, the percentage of monomer flowing out with the product is substantially reduced.

We have found that space time yields are higher and emulsions of polymerised vinyl

acetate are better, when prepared in our apparatus, than when similar emulsions are prepared by other means.

Even more important for bulk production of emulsion polymers, rates of reaction are higher and the product from our apparatus is more uniform than that available from batch reactions.

WHAT WE CLAIM IS:—

1. A continuous emulsion polymerisation apparatus which comprises a reaction vessel fitted with a stirrer of the type hereinbefore described, which vessel is equipped adjacent to the stirrer with inlets for fine streams of fluid and with an outlet.

2. An apparatus as claimed in Claim 1 in which the inlets are at opposite ends of the stirrer and the outlet is at one end of the vessel.

3. An apparatus as claimed in Claim 1 or Claim 2 in which the reaction vessel is a vertical cylinder and the outlet is at the bottom of the cylinder.

4. An apparatus as claimed in any one of the above claims in which the vessel is equipped with a reflux condenser and with heating or cooling means.

5. An apparatus as claimed in any one of the above claims in which the stirrer consists of a plurality of discs or annular rings on a shaft, the design and peripheral speed of the stirrer being such that a number of Taylor rings is formed.

6. A continuous emulsion polymerisation apparatus substantially as described herein by reference to the drawings accompanying the complete and provisional specifications.

7. A process of continuous emulsion polymerisation in which monomer and catalyst streams are fed into a reaction vessel and mixed by counterflow and in a vertical series of Taylor rings produced by stirring the contents of the vessel, the polymer dispersion being withdrawn through an outlet at the bottom of the reaction vessel.

8. A process as claimed in Claim 7 in which the polymer dispersion passes through a zone, at the bottom of the reaction vessel, in which no further monomer is added, the monomer inlet being adjacent to the lowest Taylor ring.

9. Polymer emulsions prepared substantially as described herein by reference to the examples.

ALFRED O. BALL.

Agent for the Applicants.

PROVISIONAL SPECIFICATION

Emulsion Polymerisation Apparatus

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House, Millbank, London, S.W.1, do hereby declare this invention to be described in the following statement:—

This invention provides an apparatus in which continuous emulsion polymerisation may be carried out.

Our invention provides a continuous emulsion polymerisation apparatus which comprises

a vertical cylindrical reaction vessel fitted with a concentric symmetrical stirrer which vessel is equipped at its upper and lower ends, adjacent to the stirrer, with inlets for fine streams of fluid and at its lower end below the lower inlet with an outlet pipe.

In one form of our invention the upper end of the reaction vessel is also equipped with a reflux condenser. In addition, or alternatively, the vessel may be fitted with a jacket through which heating or cooling fluid may be passed.

In a preferred form of our invention the peripheral speed of the stirrer is such that turbulent flow and hence mixing occurs close to the stirrer but farther away from the stirrer near the surface of the reaction vessel there is a type of laminar flow.

One form of our apparatus is shown in the accompanying diagram.

A cylindrical reaction vessel 1 is fitted with a rotating cylinder stirrer 2, supported on bearings 3 and 4. The cylinder 2 can be rotated by turning a shaft 5. The vessel 1 is equipped with upper and lower jets 7 and 6 respectively, an exit pipe 8 and a reflux condenser (not completely shown) 9. The vessel 1 is surrounded by a jacket 11 with entry and exit pipes 10 and 12. This jacket can be used to circulate fluid to supply or remove heat from the reaction vessel 1.

The dimensions of our apparatus are obviously dependent on the output of emulsion required and we have found that suitable stirring can be obtained when a stirrer of diameter 1.5 inches is rotated in a vessel of internal diameter 2.3 inches at between 500 and 1500 r.p.m. and all the following examples were carried out in an apparatus having those dimensions.

Solids	-	-	-	-	-	-	-	42%
Viscosity	-	-	-	-	-	-	-	1.5—2 poise (Ultraviscoson)
Particle size	-	-	-	-	-	-	-	0.75—1.0 μ
Average time of contact	-	-	-	-	-	-	-	1 hr. 50 mins.

EXAMPLE III

The vessel was thus time charged with 1 litre aqueous medium containing:—

(a) 242 parts Calasec solution (13% ammonium polymethacrylate).

25 parts Calsolene Oil (50% solution in water of sodium salt of sulphated methyl oleate).

and heated to 80° C. while stirrer was rotated at 600 r.p.m.

280 parts of an aqueous catalyst solution containing:—

(b) 25 parts Calsolene Oil

5 parts 100 volume hydrogen peroxide solution

250 parts water

were then added and pure methyl methacrylate monomer fed in at the lower jet at 4.5 ml./min. After 1.5 hours further aqueous

The method of use of our apparatus can best be explained by actual examples of its use for the preparation of stable polymer emulsions. All parts are by weight in the examples.

EXAMPLE I

With an apparatus substantially as shown in the diagram, an aqueous solution, containing 84 parts polyvinyl alcohol, 7.5 parts ammonium persulphate and 6 parts sodium carbonate in 1247 parts of water, was added to the vessel 1 through the jet 7. Vinyl acetate was added through the jet 6. By passing water through the jacket 11 the reactants were maintained at about 60° C.

The cylinder 2 was rotated at 600 r.p.m. and was breaking up the filamentary streams of reactants entering the vessel into fine particles. When the apparatus reached a state of equilibrium, i.e., material was flowing from the outlet 8 at the same rate as reactants were being added to the substantially full vessel the constants of the emulsion emerging from the outlet 8 were determined. The rate of addition of monomer and solution at equilibrium were 3.6 and 3.75 parts/min, respectively. The solids content of the polymer emulsion discharge from the outlet 8 was approximately 50% by weight, the monomer content 0.5% and the viscosity 2—3 poise (measured by an Ultraviscoson). The average particle size was 0.5 μ and the average contact time was 2 hours 20 minutes.

EXAMPLE II

Example I was repeated this time with the speed of rotation of the stirrer increased to 1150 r.p.m. The flow rates into the vessel of monomer and solution were 3.7 parts and 6.2 parts/min. respectively. The constants of the product were:—

medium (a) to which had been added 20 ml. 100 volume hydrogen peroxide was fed at 3 $\frac{1}{2}$ ml./min.

After 3 $\frac{1}{2}$ hours from catalyst solution addition the creamy emulsion leaving contained 48.4% solids. The average particle size was about 0.75 μ and the viscosity 0.4 poise (Ultraviscoson).

When a state of equilibrium has been reached in our apparatus the mechanism of reaction is thought to be as follows. As stated earlier the streams from the jets are rapidly broken down to fine particles by the rotating stirrer. Now since the aqueous solution which enters via the upper jet is heavier than the monomer which enters through the lower jet countercurrent flow develops and polymerisation proceeds. The polymer formed is heavier than the monomer and so the polymer par-

5 ticles drop to the bottom of the vessel and pass out through the exit 8. Since the orifice of the jet 6 is substantially higher than the exit 8 very little monomer is mixed with the product.

10 From the above it will be appreciated that many monomers can be polymerised in our apparatus provided suitable catalysts, flow rates, temperatures and stirring speeds are chosen. Typical examples of these have been given in the examples above and others include styrene and vinyl toluene.

15 The design of suitable apparatus in which emulsion polymerisation may be carried out in accordance with our invention can be changed in various ways from that shown in the accompanying diagram. For example, it is possible to substitute for the fluid inlet jets shown sinter plates which produce fine
20 streams of particles of fluid. The stirrer may be modified provided the stirring conditions

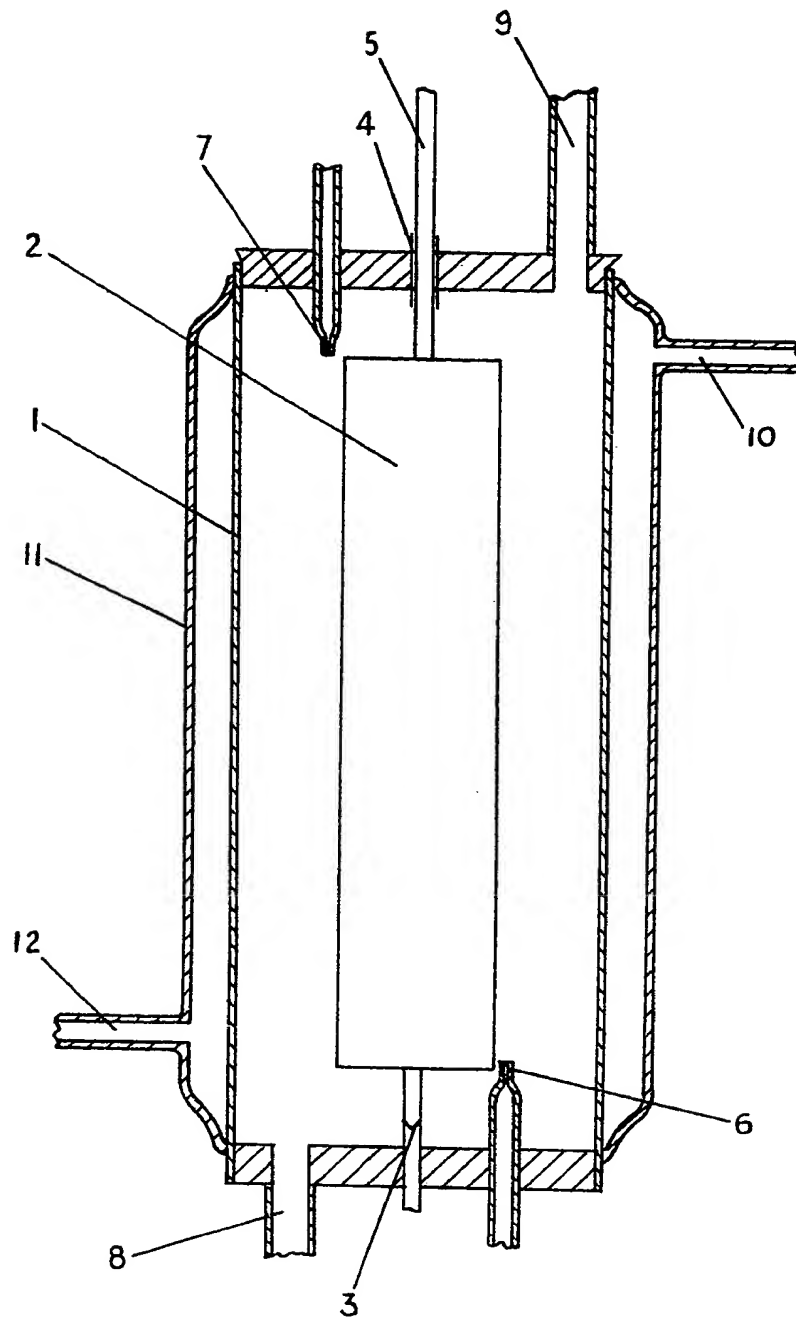
detailed above still obtain. By increasing the distance between the lower inlet and the outlet pipe, for example, by raising the lower jet relative to the stirrer, the amount of monomer flowing out with the product is substantially reduced. 25

We have found that emulsions of polymerised vinyl acetate are better, when prepared in our apparatus, than similar emulsions prepared by other means. Our polymer emulsions are particularly stable and free from gel particles. 30

Even more important for bulk production of emulsion polymers—the product from our apparatus is of smaller particle size range than that obtainable from batch reactions so improving the uniformity of the emulsion produced. 35

ALFRED O. BALL,
Agent for the Applicants.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of
the Original on a reduced scale.

